Fugacity and activity coefficient for Van der Waals mixture

ESM 5/5/21

$\underline{v}$ = molar volume; $\bar{v}$ = Partial molar volume
V = extensive volume.

By definition:

$$\ln \phi_i = \ln \frac{f_i}{x_i P} = \frac{1}{RT} \int_0^P \left(\bar{v}_i - \bar{v}_i^{IG} \right) dP \qquad (1)$$

where ϕ_i is the mixture fugacity coefficient of component i, f_i is the fugacity of component i, $\bar{v}_i$ is the partial molar volume of i and the superscript "IG" refers to an ideal gas.

we wish to integrate over V for most cubic EOS.

$$\bar{v}_i \, dP = \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} dP \qquad (2)$$

where V is the total volume of the system.

using the triple product rule

$$\left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} \left(\frac{\partial P}{\partial V} \right)_{T,N_i,N_j} \left(\frac{\partial N_i}{\partial P} \right)_{T,V,N_j} = -1 \qquad (3)$$

$$\boxed{\therefore \underbrace{\left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} dP}_{= \bar{v}_i \, dP} = -\left(\frac{\partial V}{\partial P} \right)_{T,N_i,N_j} \left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_j} dP} \qquad (4)$$

$$dV = \left(\frac{\partial V}{\partial P}\right)_{T, N_i, N_j} dP \qquad (5)$$

So eq'n (4) can be written

$$\bar{V}_i \, dP = \left(\frac{\partial V}{\partial N_i}\right)_{T, P, N_j} dP = -\left(\frac{\partial P}{\partial N_i}\right)_{T, V, N_j} dV \qquad (6)$$

$dV = N \, d\underline{V}$ where N = total moles and $\underline{V}$ is molar volume.

We need one more identity:

$$\frac{1}{\underline{V}} d(P\underline{V}) = \frac{P}{\underline{V}} d\underline{V} + dP \qquad (7)$$

$$\therefore \quad dP = \frac{1}{\underline{V}} d(P\underline{V}) - \frac{P}{\underline{V}} d\underline{V} \qquad (8)$$

$$z = \frac{P\underline{V}}{RT} \Rightarrow dP = \frac{RT}{\underline{V}} dz - \frac{P}{\underline{V}} d\underline{V}$$

$$\boxed{dP = \frac{P}{z} dz - \frac{P}{\underline{V}} d\underline{V}} \qquad (9)$$

Going back to eq'n (1):

$$\ln \phi_i = \ln \frac{f_i}{x_i P} = \frac{1}{RT} \int_0^P \left(\bar{V}_i - \bar{V}_i^{IG}\right) dP$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j} = -\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j}\left(\frac{\partial V}{\partial P}\right)_{T,N_j} \quad (10)$$

$$\bar{V}_i^{IG} = \frac{RT}{P} \quad (11)$$

substitute (10) and (11) into (1):

$$\ln\frac{f_i}{x_i P} = \frac{1}{RT}\int_0^P \left[-\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j}\underbrace{\left(\frac{\partial V}{\partial P}\right)_{T,N_j}}_{\uparrow \text{ EQ'N (5)}} - \frac{RT}{P}\right] dP \quad (12)$$

$$dV = \left(\frac{\partial V}{\partial P}\right)_{T,N_i,N_j} dP$$

$$\ln\phi_i = -\frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{\partial P}{\partial N_i}\right)_{T,\underline{V},N_j} N\,d\underline{V} + \int_0^P \underbrace{-\frac{1}{P}\,dP}_{\uparrow \text{ EQ'N (9)}} \quad (13)$$

$$dP = \frac{P}{z}\,dz - \frac{P}{\underline{V}}\,d\underline{V}$$

$$\ln\phi_i = -\frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{\partial P}{\partial N_i}\right)_{T,\underline{V},N_j} N\,d\underline{V} - \int \frac{1}{P}\left[\frac{P}{z}\,dz - \frac{P}{\underline{V}}\,d\underline{V}\right]$$

$$= -\frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} N\,d\underline{V} + \int_{\underline{V}=\infty}^{\underline{V}}\frac{1}{\underline{V}}\,d\underline{V} - \int_{\substack{P=0\\ z=1}}^{z}\frac{1}{z}\,dz \quad (14)$$

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$$\ln \phi_i = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}} \left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} \right] dV + \int_{\underline{V}=\infty}^{\underline{V}} \frac{1}{\underline{V}}\, d\underline{V} - \int_{z=1}^{z} \frac{1}{z}\, dz$$

$$\boxed{\ln \phi_i = \ln \frac{f_i}{x_i P} = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}} \left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,\underline{V},N_j} \right] d\underline{V} - \ln z \qquad (15)}$$

This form can now be used for VDW EOS.

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2} \qquad (16)$$

<u>mixing rules</u>

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (17)$$

$$b = \sum_i x_i b_i \qquad (18)$$

write (16) using extensive volume and moles

$$P = \frac{NRT}{V-Nb} - \frac{N^2 a}{V^2} = \frac{NRT}{V-\sum N_i b_i} - \frac{\sum\sum N_i N_j a_{ij}}{V^2} \qquad (19)$$

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$$\left(\frac{\partial P}{\partial N_i}\right)_{\underline{V}} = \frac{RT}{V - \Sigma N_i b_i} - \frac{NRT}{(V - \Sigma N_i b_i)^2}(-b_i) - \frac{2\,\Sigma N_j a_{ij}}{V^2}$$

$$\left(\frac{\partial P}{\partial N_i}\right)_{\underline{V}} = \frac{RT}{V - Nb} + \frac{NRTb_i}{(V-Nb)^2} - 2\,\frac{\Sigma N_j a_{ij}}{V^2} \qquad (20)$$

Eqn (15) needs $N\left(\frac{\partial P}{\partial N_i}\right)_V$, so...

$$N\left(\frac{\partial P}{\partial N_i}\right)_{\underline{V}} = \frac{RT}{\underline{V} - b} + \frac{RTb_i}{(\underline{V}-b)^2} - 2\,\frac{\Sigma x_j a_{ij}}{\underline{V}^2} \qquad (21)$$

Substitute into (15)

$$\ln \phi_i = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}} \left[\frac{RT}{\underline{V}} - \frac{RT}{(\underline{V}-b)} - \frac{RTb_i}{(\underline{V}-b)^2} + \frac{2\,\Sigma x_j a_{ij}}{\underline{V}^2}\right] d\underline{V} - \ln Z \qquad (22)$$

integrate from $\underline{V}=\infty \to \underline{V} = \frac{ZRT}{P}$

$$\ln \phi_i = \frac{1}{RT}\left\{\left[RT\ln\left(\frac{\underline{V}}{(\underline{V}-b)}\right)\right]\Bigg|_{\underline{V}=\infty}^{\underline{V}=ZRT/P} + \frac{RTb_i}{(\underline{V}-b)}\Bigg|_{\underline{V}=\infty}^{\underline{V}=ZRT/P} - \frac{2\,\Sigma x_j a_{ij}}{\underline{V}}\Bigg|_{\underline{V}=\infty}^{ZRT/P}\right] - \ln Z \qquad (23)$$

$$\ln \phi_i = \ln \left[\frac{\frac{zRT}{P}}{\frac{zRT}{P} - b} \cdot \frac{\left(\frac{P}{RT}\right)}{\left(\frac{P}{RT}\right)} \right] + \frac{b_i}{\frac{zRT}{P} - b} \cdot \frac{\left(\frac{P}{RT}\right)}{\left(\frac{P}{RT}\right)} \quad \frac{6}{9}$$

$$- \frac{2\sum x_j a_{ij}}{RT \cdot \frac{zRT}{P}} - \ln z \qquad (24)$$

Define $B_i \equiv \frac{P b_i}{RT}$, $B \equiv \frac{P b}{RT}$

Note: $\frac{zRT}{P} = \underline{V}$

$$\ln \phi_i = \ln \frac{z}{z-B} + \frac{B_i}{z-B} - \frac{2\sum x_j a_{ij}}{RT\underline{V}} - \ln z \qquad (25)$$

or finally...

$$\boxed{\ln \phi_i = \ln \frac{f_i}{x_i P} = \frac{B_i}{z-B} - \ln(z-B) - \frac{2\sum_j x_j a_{ij}}{RT\underline{V}}} \qquad (26)$$

To write each term wrt z:

$$A_{ij} \equiv a_{ij} \frac{P}{(RT)^2}$$

$$\boxed{\ln \phi_i = \frac{B_i}{z-B} - \ln(z-B) - \frac{2\sum_j A_{ij}}{z}} \qquad (27)$$

We can also compute the activity coefficient of species i in a mixture:

$$f_i = \gamma_i x_i f_i^o \qquad (27)$$

superscript o = pure fluid.

where γ_i is the activity coefficient and f_i^o = pure i fugacity

From (26)

$$f_i = x_i P \exp\left[\frac{B_i}{Z-B} - \ln(Z-B) - \frac{2\sum_j x_j A_{ij}}{Z}\right]$$

$\uparrow$ mixture (28)

$f_i^o = ?$ Derive in similar manner as for mixture.

Pure fluid: (Assume vapor, no phase change)

$$\ln\frac{f^o}{P} = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{RT}{\underline{V}} - P\right)d\underline{V} - \ln Z^o + (Z^o - 1) \qquad (29)$$

Integrate 1st term in (29)

$$\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{RT}{\underline{V}} - P\right)d\underline{V} = \int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{RT}{\underline{V}} - \frac{RT}{\underline{V}-b} + \frac{a}{\underline{V}^2}\right)d\underline{V}$$

$$= RT\ln\left(\frac{\underline{V}}{\underline{V}-b}\right) - \frac{a}{\underline{V}} \quad ✓ \qquad (30)$$

Substitute into (2a)

$$\ln \frac{f^0}{P} = \ln \frac{\underline{V}}{\underline{V} - b} - \frac{a}{RT\underline{V}} + (z^0 - 1) - \ln z^0 \quad (31)$$

$$\ln \frac{f^0}{P} = \ln\left(\frac{z^0}{z^0 - \frac{Pb}{RT}}\right) - \frac{a}{RT\underline{V}} \cdot \left(\frac{RT}{P} \cdot \frac{P}{RT}\right) + (z^0 - 1) - \ln z^0 \quad (32)$$

multiply top and bottom by P/RT

$$B \equiv \frac{Pb}{RT} \qquad A \equiv \frac{aP}{(RT)^2}$$

$$\ln \frac{f^0}{P} = \ln z^0 - \ln(z^0 - B) - \frac{A}{z^0} + (z^0 - 1) - \ln z^0 \quad (33)$$

Note:

vdW EOS $\quad P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2}$

$$z^{vdW} = \frac{P\underline{V}}{RT} = \frac{\underline{V}}{\underline{V} - b} - \frac{a}{RT\underline{V}}$$

Finally

$$\boxed{\ln \frac{f^0}{P} = (z^0 - 1) - \frac{A}{z^0} - \ln(z^0 - B)} \quad (34)$$

From (34)

<u>Pure i</u>

$$f_i^o = P \exp\left[(Z^o - 1) - \ln(Z^o - B_i) - \frac{A_{ii}}{Z^o} \right] \tag{35}$$

combine 27, 28, 35

$$\boxed{\frac{f_i}{x_i f_i^o} = \gamma_i = \frac{\exp\left\{ \left[\frac{B_i}{(Z-B)}\right] - \ln[Z-B] - \left[\frac{2\sum_j x_j A_{ij}}{Z}\right] \right\}}{\exp\left\{ [Z^o - 1] - \ln[Z^o - B_i] - \frac{A_{ii}}{Z^o} \right\}}} \tag{36}$$

* This should give γ_i, but top term is for the mixture and bottom term is for pure. Z in mixture not necessarily same as Z^o pure fluid.